

EQUIVALENT TO CITATION 2

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



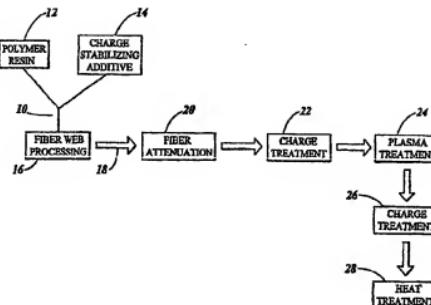
(43) International Publication Date
1 February 2001 (01.02.2001)

PCT

(10) International Publication Number
WO 01/07144 A2

- | | | |
|--|---|---|
| (51) International Patent Classification: | B01D 39/16 | (81) Designated States (<i>national</i>): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KB, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, T1, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW. |
| (21) International Application Number: | PCT/US00/19279 | (84) Designated States (<i>regional</i>): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SI, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TI, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). |
| (22) International Filing Date: | 14 July 2000 (14.07.2000) | |
| (25) Filing Language: | English | |
| (26) Publication Language: | English | |
| (30) Priority Data: | 09/359,348 21 July 1999 (21.07.1999) US | |
| (71) Applicant (<i>for all designated States except US</i>): ROLLINGSWORTH & VOSE COMPANY [US/US]; 112 Washington Street, East Walpole, MA 02092 (US). | | |
| (72) Inventor; and | Published: — With international search report. — Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments. | |
| (75) Inventor/Applicant (<i>for US only</i>): GAHAN, Richard, E. [US/US]; 10 Saddleback Drive, Wrentham, MA 02093 (US). | | |
| (74) Agents: ROTHENBERGER, Scott, D. et al.; Nutter, McClennen & Fish, LLP, One International Place, Boston, MA 02110-2699 (US). | For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette. | |

(54) Title: PLASMA TREATED ELECTRET FILTER MEDIA



WO 01/07144 A2

(57) Abstract: An electret filter media includes an additive or mixtures thereof that enhance the charge stability of the media. The filter media achieves acceptable alpha values for a range of filtration challenges without significant decay in alpha values over time. Preferred charge additives include fatty acid amides and mixtures thereof.

PLASMA TREATED ELECTRET FILTER MEDIA**Background of the Invention**

This invention relates to electret filter media having enhanced charge stability.

Electret filter media have long been used in many filtration applications. Electret filter media are those that include a dielectric insulating polymer web that is treated to possess substantially permanent spatially oriented, opposite charge pairs or dipoles. Among the common polymer webs used for electret filter media are polypropylene, polyethylene, polyester, polyamide, polyvinyl chloride, and polymethyl methacrylate.

Conventional filter media are substantially lacking in electrostatic charge and rely upon impingement, impaction and diffusion for filter performance. Electret filter materials offer improved filtering performance over conventional filter materials. The presence of oriented dipoles in the electret filter media is believed to enhance filter performance by allowing the filter media to attract and retain charged and uncharged particles to be filtered.

Electret filter materials are made by a variety of known techniques. One technique for manufacturing electret filter media involves extruding a polymer, typically having a high melt flow index, through a die having a linear array of orifices. An air knife is used to attenuate the extruded polymer fibers by a ratio of about 300:1. The attenuated fibers, having diameters of about one to ten micrometers, are collected on a rotating drum or moving belt using a moderate vacuum. The fiber web is then treated to impart on the fiber web charge pairs or dipoles. The charge pairs or dipoles can be imparted to the fiber, for example, using AC and/or DC corona discharge.

One problem associated with electret filter material is that the charge pairs or dipoles imparted to the filter media often are not stable. In some instances, charge or its spatial orientation is lost after filtering certain contaminants for relatively short time periods. The result is a marked decrease in filter performance over a relatively short period of time (e.g., less than 20 minutes). The National Institute of Safety and Health (NIOSH) has established standards for performance of certain filters. The NIOSH standards evaluate filters in a carrier after a 200 milligram filtration challenge. One challenge, of solid aerosol particles, evaluates filter performance against solid sodium chloride particles suspended in air. Another challenge, of liquid aerosol particles, evaluates filter performance against liquid droplets of dioctyl phthalate (DOP) suspended in air. Electret filter media generally are able to maintain charge stability and filter

performance when filtering solid aerosols, including the sodium chloride test standard. However, liquid aerosols tend to degrade the charge on the electret filter media, and thus filter performance diminishes after only a short period of filtration.

There is thus a need for electret filter media having improved charge stability that are able to maintain acceptable filter performance over time.

Summary of the Invention

The present invention circumvents the problems described above by providing a fiber web which retains particles and/or oil without significant reduction in filtration performance even after prolonged filtration challenges. In a particular embodiment, the filter media of the present invention is an oleophobic plasma treated electret polymeric fiber web that can optionally include a charge stabilizing additive, e.g., a fatty acid amide. Accordingly, the present invention provides charge stabilized electret filter media that provides enhanced filtration performance characteristics.

The filter media of the invention may be used in a variety of filtration applications, including use in industrial face masks or respirators, indoor air quality filters, surgical masks, room air cleaners, cabin airfilters, vacuum filters, HVAC filters, HEPA filters ASHRAE filters and ULPA filters. It is understood that the term "filter" as used herein encompasses any device with which filter media of the invention may be used to filter air and/or other gases.

The invention provides filter media having a melt blown hydrophobic and/or oleophobic plasma treated electret polymer fiber web. In one embodiment, the polymer fiber web is annealed. Typically, the hydrophobic and/or oleophobic plasma treated electret filter media has been treated with a hydrophobic and/or oleophobic material such as an alkylene, acrylate, methacrylate, alkyl oxirane, or alkylene oxirane. These hydrophobic and/or oleophobic materials are preferably halogenated, e.g., fluorinated. A preferred hydrophobic and oleophobic alkylene is hexafluoropropylene. A preferred hydrophobic and oleophobic alkyl oxirane is hexafluoropropyl oxirane (2-trifluoromethyl-2-fluoro-3,3-difluorooxirane).

The invention also provides filter media having a melt blown hydrophobic and/or oleophobic plasma treated electret polymer fiber web including a melt processable fatty acid amide present within the web. Typically, the amide is present at a concentration in a

range from about 0.01% to about 20% by weight. In one embodiment, the filter media is annealed.

5 In another aspect, the invention is drawn to filters having filter media with a melt blown hydrophobic and/or oleophobic plasma treated electret polymer fiber web. In a preferred embodiment, the fiber web is annealed.

In still another aspect, the invention is drawn to filters having filter media with a melt blown hydrophobic and/or oleophobic plasma treated electret polymer fiber web including a melt processable fatty acid amide present within the web, wherein the amide is present at a concentration in a range from about 0.01% to about 20% by weight. In a 10 preferred embodiment, the fiber web is annealed.

In yet another aspect, the invention relates to a method for manufacturing melt blown hydrophobic and/or oleophobic plasma treated electret polymer media. A web of melt blown polymer fibers is treated to form substantially permanent charge pairs or dipoles in the melt blown polymer web. The polymer web is treated with a plasma 15 having hydrophobic and/or oleophobic reactive species, preferably with a plasma containing hexafluoropropylene reactive species. Permanent dipoles, e.g., electret characteristics, can be imparted to the web by a variety of techniques including AC corona or DC corona discharge and combination thereof. In a preferred embodiment, the manufacturing process can be modified by heat treating, e.g., annealing, the polymer 20 web.

In another aspect, the invention is drawn to a method for manufacturing electret filter media by providing a web of melt blown polymer fibers having a charge stabilizing fatty acid amide incorporated within the fibers. The polymer web is treated with a plasma having hydrophobic and/or oleophobic reactive species, preferably a plasma containing 25 hexafluoropropylene reactive species. The web is then subjected to conditions to form substantially permanent charge pairs or dipoles, electret properties, in the melt blown polymer web. Typically the fatty acid amide is present in a range between about 0.01% and about 20%. In a preferred embodiment, the manufacturing process can be modified by heat treating, e.g., annealing, the polymer web.

30 The electret polymer fiber web can be made from a variety of polymeric materials, including polypropylene, polyester, polyamide, polyvinyl chloride, polymethylmethacrylate, and polyethylene. Polypropylene is among the more preferred polymeric materials. Typically, the polymer fibers that form the web have a diameter in

the range of about 1 to 20 micrometers and the weight of the polymer fiber web is in the range of about 10 to 520g/m².

The electret filter media of this invention is characterized by improved filtration performance and enhanced charge stability of the electret polymer web. In particular, the filter media is able to provide desirable filtration properties, as indicated by alpha value, despite continued filtration challenge. In one embodiment, the filter media meets the NIOSH standard for class P 95 nonwoven filter media. In another embodiment, the filter media meets the NIOSH standard for class P 99 nonwoven filter media. Preferably, the filter media meets the NIOSH standard for class P 100 nonwoven filter media.

Other advantages of the invention will be readily apparent to one having ordinary skill in the art upon reading the following description.

All percentages by weight identified herein are based on the total weight of the web unless otherwise indicated.

15 Brief Description of the Drawings

Other objects, advantages and features of the present invention will be readily appreciated as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings, in which like reference numerals designate like parts throughout the figures thereof and wherein:

20 FIG. 1 is a flow chart illustrating a process for manufacturing plasma treated electret filter media according to the invention.

Detailed Description of the Invention

25 The features and other details of the invention will now be more particularly described and pointed out in the claims. It will be understood that the particular embodiments of the invention are shown by way of illustration and not as limitations of the invention. The principle features of this invention can be employed in various embodiments without departing from the scope of the invention.

30 The present invention is based, at least in part, on the discovery of an electret filter media with improved charge stability. The charge stability is manifested by acceptable alpha levels, with minimal alpha decay, when the filter media are subjected to solid and/or liquid aerosol challenges. In instances where alpha decay occurs, the final alpha value is still indicative of acceptable filter performance. The filter media of the invention

include a hydrophobic and/or oleophobic, plasma treated electret polymer fiber web that optionally can include at least one charge stabilizing additive, e.g., a fatty acid amide, or mixtures of two or more fatty acid amides. In preferred embodiments, the fiber web is annealed.

5 The use of reactive or excited gases in the treatment of fibers, e.g., nonwovens, provides a method for treating surfaces with energetic species which react with the substrate. For example, by changing the surface chemistry of the fiber(s), materials which would otherwise be incompatible with a variety of host materials may be rendered compatible therewith. Plasmas can be used to deposit hydrophobic and/or oleophobic 10 coatings on nonwovens to increase filter performance, such as, retention of particles and/or oil without significant reduction in filtration performance. Treatment of nonwovens with plasma activated species eliminates many of the disadvantages associated with ordinary gas treatment processes and provides results that are otherwise unobtainable.

15 The term "hydrophobic" is used herein to describe nonwoven webs of the invention which are not wet by liquid water or aqueous body fluids such as blood, saliva, perspiration and urine, and which are capable of repelling and preventing the passage of liquid water through their structure.

20 The term "oleophobic" is used herein to describe nonwoven webs of the invention which are not wet by oils, greases or body fluids which contain oily components such as perspiration and are capable of preventing the passage of oils and greases through their structure. Therefore, oleophobic treated fiber webs of the invention have the enhanced ability to repel oils, such as DOP or mineral oil.

25 The present invention makes feasible the use of plasma activated species, e.g., monomers, to treat fibers or nonwovens in a continuous process or in a batch process, and eliminates many of the deficiencies in conventional surface treatments, e.g., coating.

30 The method in accordance with the present invention includes a step of continuously providing a plasma activated species in a treatment zone maintained at sub-atmospheric to atmospheric pressure, continuously passing a fiber web through the treatment zone thereby treating the web with plasma activated species such as fluorinated monomers.

 The term "continuous" as used herein means that the length of time that any particular portion of a nonwoven web is substantially less than the length of time that the

apparatus is in operation. Furthermore, the term "continuous" as used herein means that a nonwoven web to be treated only traverses a treatment zone containing plasma activated species once during the course of the web manipulation through a plasma apparatus. The treated nonwoven web can be re-introduced to a second plasma or can be further treated, e.g., passed through AC and/or DC corona discharge or elevated temperature(s).

5 "Plasma activated species" in accordance with the present invention contemplates reactive gaseous species that include, or result from the ionization of, an ionizable gas into a primary plasma. The term "primary plasma" indicates excited states of ionizable gas while that gas is under the direct influence of an electromagnetic field or other plasma 10 generating device and also represents the highest activated states in this reaction system. A "plasma" or "primary plasma" is created by introducing an ionizable gas into a vacuum chamber and exciting the gas with, for example, radio frequency (RF) energy. The RF energy dissociates the gas into electrons, ions, free radicals and metastable excited species. See Cormia, "Use Plasmas To Re-Engineer Your Advanced Materials," R&D 15 Magazine, Jul. 19, 1990 at page 60, the text of which is hereby incorporated by reference; See also "Plasma Polymerization," H. Yasuda, 1985, Academic Press, the contents of which are expressly incorporated herein by reference. Plasma activated species in accordance with the present invention may include, without limitation, electrons, ions, free radicals, metastable species the latter of which are commonly referred to as plasma 20 afterglow. Of course, when reference is made to "a plasma activated species," the term is understood to include at least one plasma activated species.

Various methods are known to those skilled in the art which are suitable for the generation of plasma species. These include for example, but should not be considered as limiting to this invention, low temperature plasmas, high temperature plasmas, parallel 25 plate reactors, asymmetric parallel plate reactors and glow discharge. Any method or apparatus which is capable of generating a plasma is suitable for use in the present invention. The preferred method is a low temperature, low or high vacuum plasma process.

The term "treatment zone" refers to a region within the apparatus in which the 30 nonwoven fiber web comes into contact with the primary plasma and/or other plasma activated species. In some embodiments, the nonwoven fiber web will first contact an ionizable gas. Thereafter, as the web moves into the region of influence of a plasma generating RF electrode, the web will come in contact with a primary plasma as

previously defined. The web will remain in contact with the primary plasma for the entire length of the plasma generating electrode, and possibly for some short distance thereafter.

5 Plasma treatment can be used to alter the surface, or to surface treat nonwoven fiber webs by "functionalization," "coating," or "grafting." In "functionalization," the gases that are used to create the plasma and plasma activated species cannot be polymerized. The electrons and the active species generated in the plasma by the ionization of the gas interact with the fiber or web surface. The plasma activated species are thought to extract atoms, such as hydrogen or molecules such as methyl groups, from the surface of the material, thereby leaving an active site. Active sites created on the 10 surface react with other active species to form various chemical functional groups on the fiber or web's surface.

15 The term "coating" is art recognized in that complex gases such as volatile hydrophobic and/or oleophobic monomers are introduced into a chamber and ionized. This creates various active fragments that re-combine as a film on the surface of the fiber or web and conform very accurately to the contour of the fiber or web surface.

20 The term "grafting" is art recognized and is a hybrid of plasma functionalization and conventional surface chemistry. In this process, a noble gas plasma such as argon or helium creates free radicals on the surface of the web. After plasma activation, and before exposure to the atmosphere, the web surface is exposed to, for example, a vapor of an unsaturated monomer. The free radicals on the surface react with the unsaturated monomer causing a polymer layer to be grafted on to the activated web's surface.

25 The term surface grafting is generally used in contrast to through grafting, in which grafting extends all the way through the bulk of the original polymer sample. Through grafting may be referred to as homogeneous grafting, in comparison with heterogeneous surface grafting.

30 In through grafting, the grafted polymer penetrates all the way through the substrate. In surface grafting, the penetration of grafting is limited to the vicinity of the surface, and consequently the change in properties, such as swelling of the grafted polymer in the solvent, is restricted to the vicinity of the surface. The extent of the penetration and the concentration of the grafted polymer at the surface are dependent on the conditions of the grafting reaction.

 Examination of plasma treatment procedures makes it clear that a certain degree of change in the bulk properties of the substrate polymer is expected even with surface

treatment, and the extent of change is more or less proportional to the degree of surface treatment. The surface properties of the plasma treated polymer are also affected by the plasma treatment. An increase in the degree of plasma treatment may change surface properties; however, this may be achieved without considerable alteration of the bulk properties of the substrate polymer.

- 5 Characteristic features of the plasma polymerization process used to form a composite structure are quite clear from the comparison. Plasma polymerization (on polymeric substrates) provides modification of the surface with the least alteration of the bulk properties of substrate polymers, whereas surface grafting by conventional means
10 tends to alter the bulk properties of substrate due to partial penetration of the grafting into the bulk substrate.

- 15 When plasma treating a polymeric fiber web, it is not necessary, in all applications, that the plasma treatment be uniform. In general, a plasma treatment layer as thin as 50 angstroms may be sufficient for certain applications. However, to obtain a uniform layer, generally the layer has a thickness of at least about 500 angstroms and will range up to about 1 micron in thickness. The exact thickness of the applied layer will vary with the size and composition of the fiber web being treated, the composition of the layer being applied, and the extent to which the fiber web is exposed to the primary plasma or plasma activated species.

- 20 A variety of polymeric substrates can be used for the fiber web. These include polyolefins such as polyethylene, polypropylene, polyisobutylene, and ethylene-alpha-olefin copolymers; acrylic polymers and copolymers such as polyacrylate, polymethylmethacrylate, polyethylacrylate; vinyl halide polymers and copolymers such as polyvinyl chloride; polyvinyl ethers such as polyvinyl methyl ether; polyvinylidene
25 halides, such as polyvinylidene fluoride and polyvinylidene chloride; polycrylonitrile; polyvinyl ketones; polyvinyl amines; polyvinyl aromatics such as polystyrene; polyvinyl esters, such as polyvinyl acetate; copolymers of vinyl monomers with each other and olefins, such as ethylene-methyl methacrylate copolymers, acrylonitrile-styrene copolymers, ABS resins, and ethylene-vinyl acetate copolymers; natural and synthetic
30 rubbers, including butadiene-styrene copolymers, polyisoprene, synthetic polyisoprene, polybutadiene, butadiene-acrylonitrile copolymers, polychloroprene rubbers, polyisobutylene rubber, ethylene-propylene rubber, ethylene-propylene-diene rubbers, isobutylene-isoprene copolymers, and polyurethane rubbers; polyamides such as Nylon

66 and polycaprolactam; polyesters, such as polyethylene terephthalate; polycarbonates; polyimides; polyethers; fluoropolymers such as polytetrafluoroethylene and fluorinated ethylenepropylene.

Typical gases which are used in plasma treatment of polymeric fiber webs include
5 carrier gases such as, for example, nitrogen, helium, oxygen, carbon dioxide, methane, ammonia, sulfur dioxide and nitrous oxide; noble gases; reactive monomers; and combinations thereof. Typical reactive monomers are those that contain at least one degree of unsaturation, e.g., vinyl or allyl group, e.g., alkynes, or those monomers which contain an oxirane ring (epoxides), oxetanes, or ether rings, e.g., alkyl oxiranes or 10 alkylene oxiranes. Therefore, acryl, methacryl, unsaturated amides, dienes, trienes, oxiranes, alkylene oxiranes, and oxetanes in monomeric form can be used for hydrophobic and/or oleophobic plasma polymerization with melt blown fiber web.

Particularly preferred reactive monomers include those that are halogenated (Br, I, Cl, F) and provide hydrophobicity and/or oleophobility to the treated fiber web. Suitable 15 examples of hydrophobic and/or oleophobic vinyl groups include tetrafluoroethylene, octafluorobutylene and preferably hexafluoropropylene. Examples of hydrophobic and/or oleophobic halogenated alkyl oxiranes such as tetrahaloethyleneoxide, i.e., tetrafluoroethylene oxide (2,2,3,3-tetrafluorooxirane), hexahalopropylene oxide, i.e., hexafluoropropylene oxide (2-trifluoromethyl-2-fluoro-3,3-difluorooxirane), 20 hexahalooxetanes, i.e., 2,2,3,3,4,4-hexafluorooxetane, and octahalobutylene oxide, i.e., octafluorobutylene oxide (2,2,3,3,4,4,5,5-octafluorotetrahydropyran). Examples of hydrophobic and/or oleophobic alkylene oxiranes include hexafluoroallyloxide. Suitable examples of plasma initiated treatments can be found in U.S. Pat. No. 4,845,132.

Preferred reactive monomers include unsaturated fluorocarbons such as 25 tetrafluoroethylene, hexafluoropropylene and octafluorobutylene; and organosilicons such as hexamethyldisiloxane, tetramethyldisiloxane and tetraethoxysilane. Mixtures of the aforementioned gases, such as the use of helium and hexafluoropropylene, are also contemplated. Of course, the choice of gas is virtually limitless so long as it is ionizable to form plasma activated species.

In operation, a polymeric fiber web, with or without charge stabilizing agent(s), is 30 placed into a chamber which is evacuated to a stable base pressure, generally around about 0.01 Torr through about 760 Torr (atmospheric pressure), preferably between about 0.05 to about 0.15 Torr, depending on the composition of the untreated web material.

Operating pressure is generally maintained between about 0.01 and 10.0 Torr and more preferably between about 0.01 and 1.0 Torr using a vacuum pump. The ionizable gas flow rate is maintained between about 1 and 100 liters per minute (lpm) and more preferably between about 0.1 and about 10 lpm is established and maintained.

5 Alternatively, gas flow can be measured in lpm per foot width of web material. Suitable ranges for treatment using these parameters are between 1 and 20 lpm per foot width, more preferably between about 2 to about 20 lpm per foot width, most preferably, 3 lpm per foot width.

10 The RF energy supply is energized to create a plasma and plasma activated species of the ionizable gas in the treatment chamber and, more specifically, in the treatment zone. Typically, the gas pumped into the treatment chamber includes a carrier gas, e.g. helium, and a reactive gas, e.g. a monomer. The RF energy supply provides power which generally ranges from about 50 to about 5000 watts and, more preferably from about 500 to about 3000 watts. Alternatively, power can be measured in watts per 15 foot width of web material. Suitable ranges for treatment using these parameters are between 100 and about 1000 watts per foot width, preferably between about 500 and about 750 watts per foot width, most preferably at about 650 watts per foot width.

20 The polymeric web is fed through the plasma treatment chamber at about 1 (foot per minute (fpm)) to about 100, preferably between about 15 to about 30 fpm. These parameters may vary widely as the dimensions of the apparatus change to accommodate, for example, a higher throughput. As web width increases, pressures, flow rates of ionizable gases, and power levels will have to be scaled up accordingly. For example, speed is dependent on reactor design such as power and electrode area. A preferred speed utilized to produce fiber webs of the invention was one which provides 45 seconds to 1 25 minute of residence time in the plasma chamber.

Typically, the plasma is generated by use of radio frequency or microwave energy as is known in the art.

30 The polymeric web can be further treated to have electret properties and can be prepared as disclosed in U.S. Patent Application 09/335,002, entitled "Charge Stabilized Electret Filter Media," by Stephen T. Cox, filed on June 17, 1999, the contents of which are incorporated herein by reference. A variety of techniques are well known to impart a permanent dipole to the polymer web in order to form electret filter media. Charging can be effected through the use of AC and/or DC corona discharge units and combinations

thereof. The particular characteristics of the discharge are determined by the shape of the electrodes, the polarity, the size of the gap, and the gas or gas mixture. In one embodiment charging can be accomplished solely through the use of an AC corona discharge unit. In another embodiment it is useful to use both AC and DC corona

- 5 discharge units. In a preferred technique the polymer web is first subjected to AC corona discharge followed by one or more successive treatments by a DC corona discharge unit. Charging can also be accomplished using other techniques, including friction-based
10 charging techniques. Typically the fiber web is subjected to a discharge of between about 1 to about 30 kV(energy type, e.g., DC discharge or AC discharge)/cm, preferably between about 10 kV/cm and about 30 kV/cm, with a preferred range of between about 10 to about 20 kV/cm.

It will be appreciated by one skilled in the art that corona unit(s), AC corona discharge unit(s) and/or DC corona discharge unit(s) can be placed above and/or below a meltblown fiber web to impart electret properties to the fiber web. Configurations

- 15 include placement of a neutrally grounded roll(s) on either side of the fiber web and the active electrode(s) above or below either side of the web. In certain embodiments, only one type of corona discharge unit, e.g., a DC or an AC corona discharge unit, is placed above, below or in an alternating arrangement above and below the fiber web. In other embodiments alternating AC or DC corona discharge units can be used in combination.
20 The AC or DC corona discharge unit can be controlled so that only positive or negative ions are generated.

In one embodiment, a permanent dipole can be imparted to the polymer fiber web as follows. The web is first charged using an AC corona, followed by a charging with a series of DC corona discharge units, e.g., DC charge bars. The DC corona discharge units are positioned on alternating sides of the passing fiber web and each successive DC corona discharge unit applies a charge of a different polarity, i.e., positive/negative. In a preferred embodiment, the charge of the DC corona discharge units located above and below the nonwoven web alternates from positive to negative in a series of treatments, e.g., 2, 4, 6, etc. Alternatively, the DC corona discharge units are positive or negative and do not alternate in charge.

An example of a process for producing electret properties in fiber webs can be found in U.S. Patent No. 5,401,446, the contents of which are incorporated herein by reference.

The invention therefore provides filter media having a melt blown hydrophobic and/or oleophobic plasma treated electret polymer fiber web. In one embodiment, the polymer fiber web is annealed. Typically, the hydrophobic and/or oleophobic plasma treated electret filter media has been treated with a plasma which contains reactive plasma species such as hydrophobic and/or oleophobic alkylene, acrylate, or methacrylate species which are preferably halogenated, e.g., fluorinated. A preferred hydrophobic and oleophobic alkylene is hexafluoropropylene. A preferred hydrophobic and oleophobic oxirane is hexafluoropropylene oxirane.

The invention also provides filter media having a melt blown hydrophobic and/or oleophobic plasma treated electret polymer fiber web including a melt processable fatty acid amide present within the web. Typically, the amide is present at a concentration in a range from about 0.01% to about 20% by weight. The hydrophobic and/or oleophobic plasma treated electret filter media has been treated with a plasma which contains reactive plasma species such as an oleophobic and/or hydrophobic alkylene, acrylate, or methacrylate species which are preferably halogenated, e.g., fluorinated. In one embodiment, the filter media is annealed.

In another aspect, the invention is drawn to filter devices in which the filter media is a melt blown hydrophobic and/or oleophobic plasma treated electret polymer fiber web. In a preferred embodiment, the fiber web is annealed.

In still another aspect, the invention is drawn to filter devices in which the filter media is a melt blown hydrophobic and/or oleophobic plasma treated electret polymer fiber web including a melt processable fatty acid amide, e.g., a charge stabilizing additive, present within the web, wherein the amide is present at a concentration in a range from about 0.01% to about 20% by weight. In a preferred embodiment, the fiber web is annealed.

Examples of charge stabilizing additives include fatty acid amides derived from fatty acids. The term "fatty acid" is recognized by those having ordinary skill in the art and it is intended to include those saturated or unsaturated straight chain or branched chain carboxylic acids obtained from the hydrolysis of fats. Examples of suitable fatty acids include lauric acid (dodecanoic acid), myristic acid (tetradecanoic acid), palmitic

acid (hexadecanoic acid), stearic acid (octadecanoic acid), oleic acid ((Z)-9-octadecenoic acid), linoleic acid ((Z,Z)-9,12-octadecadienoic acid), linolenic acid ((Z,Z,Z)-9,12,15-octadecatrienoic acid) and eleostearic acid (Z,E,E)-9,11,13-octadecatrienoic acid).

Typically the amides formed from the above referenced acids are primary amides which are prepared by methods well known in the art.

Secondary and tertiary fatty acid amides are suitable as charge stabilizing agents wherein the amide nitrogen is substituted with one or more alkyl groups. Secondary and tertiary fatty acid amides can also be prepared by methods well known in the art, such as by esterification of a fatty acid followed by an amidation reaction with a suitable alkylamine. The alkyl substituents on the amide nitrogen can be straight chain or branched chain alkyl groups and can have between about two and twenty carbon atoms, preferably between about two and 14 carbon atoms, more preferably between about two and six carbon atoms, most preferably about two carbon atoms. In a preferred embodiment, the fatty acid amide can be a "bis" amide wherein an alkyl chain tethers two nitrogens of two independent amide molecules. For example, alkylene bis-fatty acid amides include alkylene bis-stearamides, alkylene bis-palmitamides, alkylene bis-myristamides and alkylene bis-lauramides. Typically the alkyl chain tether includes between about 2 and 8 carbon atoms, preferably 2 carbon atoms. The alkyl chain tether can be branched or unbranched. Preferred bis fatty acid amides include ethylene bis-stearamides and ethylene bis-palmitamides such as N,N'-ethylenebistearamide and N,N'-ethylenebispalmitamide.

In certain embodiments, the charge stabilizing additive, e.g., a fatty acid amide, can be present within the polymer fiber web at a concentration in the range of about 0.01 to about 20% by weight. In other embodiments, the charge stabilizing additive can be present within the polymer fiber web at a concentration in the range of about 2.0% to about 20% by weight. A preferred concentration range for the fatty acid amide charge stabilizing additive is in the range of about 5% to about 11% by weight of the web, preferably between about 1% and about 8%. The ranges of concentrations intermediate to those listed are also intended to be part of this invention, e.g., about 2.5% to about 17%, 4.0% to about 15%, and about 6.0% to about 12.0% by weight. For example, ranges of concentration using a combination of any of the above values recited as upper and/or lower limits are intended to be included, e.g., 1% to about 6%, 2.5 to about 12%, etc.

One group of useful charge stabilizing additives, as noted above, are fatty acid amides. Examples of preferred fatty acid amides include stearamide and ethylene bis-stearamide. An exemplary stearamide is commercially available as UNIWAX 1750, available from UniChema Chemicals, Inc. of Chicago, Illinois. ACRAWAX® C is an ethylene bis-stearamide which is commercially available from Lonza, Inc. of Fair Lawn, New Jersey. ACRAWAX® C contains N, N'-ethylenebisstearamide (CAS No. 110-30-5) and N,N'-ethylenebispalmitamide (CAS No. 5518-18-3) with a mixture of C-14 to C-18 fatty acid derivatives (CAS No. 67701-02-4) with an approximate ratio of 65/35/2 (N, N'-ethylenebisstearamide/N,N'-ethylenebispalmitamide/ mixture of C-14 to C-18 fatty acid derivatives) by weight. For example, the commercial product includes N,N'-ethylenebisstearamide, N,N'-ethylenebispalmitamide with C14-C18 fatty acids. In certain embodiments of the invention, either N,N'-ethylenebisstearamide or N,N'-ethylenebispalmitamide can be the sole charge stabilizing additive. In another embodiment, the ratio of a C14-C18 fatty acid can be varied from between about 0 to 20% based on the total amount of the bisamides. In still other embodiments, mixtures of N,N'-ethylenebisstearamide and N,N'-ethylenebispalmitamide which fall in the range between about 0 to 100% for each bisamide can be utilized as additive mixtures, e.g., 80/20, 70/30, 5/50, etc.

The polymers used to form the fibers of the web can be selected from among many suitable polymers. Examples of these polymers include polyethylene, polyester, polyamide, polyvinyl chloride, and polymethyl methacrylate and, preferably, polypropylene.

One of ordinary skill in the art will appreciate that melt blown webs are comprised of filters having a relatively broad distribution of fiber diameters. The average fiber diameter of the polymer used to form the polymer fiber web generally is in the range of about 1 to about 20 micrometers. Depending on the intended application, a more preferred average polymer fiber diameter is in the range of about 1 to about 15 micrometers, more preferably between about 2 to about 4 micrometers.

The web basis weight of the polymer fiber web will vary depending upon the requirements of a given filtering application. In general, higher web basis weights yield better filtration, but there exists a higher resistance, or pressure drop, across the filter barrier when the filter media has a higher basis weight. For most applications the web basis weight can be in the range of between about 10 to about 520 g/m². Preferably the

5 web weight is in the range of between about 30 to about 400 g/m², more preferably between about 30 to about 200 g/m². One of ordinary skill in the art can readily determine the optimal web basis weight, considering such factors as the desired filter efficiency and permissible levels of resistance. Furthermore, the number of plies of the polymer fiber web used in any given filter application can also vary from approximately 1 to 10 plies. One of ordinary skill in the art can readily determine the optimal number of plies to be used.

10 Filter performance is evaluated by different criteria. It is desirable that filters, or filter media, be characterized by low penetration across the filter of contaminants to be filtered. At the same time, however, there should exist a relatively low pressure drop, or 15 resistance, across the filter. Penetration, often expressed as a percentage, is defined as follows:

$$\text{Pen} = C/C_0$$

15 where C is the particle concentration after passage through the filter and C₀ is the particle concentration before passage through the filter. Filter efficiency is defined as

$$100 - \% \text{ Penetration.}$$

Because it is desirable for effective filters to maintain values as low as possible for both penetration and pressure drop across the filter, filters are rated according to a value termed alpha (α), which is the slope of log penetration versus pressure drop across the 20 filter. Steeper slopes, or higher alpha values, are indicative of better filter performance. Alpha is expressed according to the following formula

$$\alpha = -100 \log (C/C_0)/D P,$$

where D P is the pressure drop across the filter.

In many filtering situations it is important to have a high initial alpha value. 25 However, it is equally, if not more important, to maintain acceptable alpha values well into the filtration process. Decaying alpha values is, as noted above, a problem often encountered in certain filtration procedures. In many instances it is thus important to achieve acceptable alpha values well into the filtering process. Some standard tests for evaluating filter performance focus on penetration and resistance (as related by alpha 30 value) after 200 milligrams of loading. Alpha decay is generally not a problem in filtering gases that contain only solids. In fact, in such filtering applications the alpha value often increases over time. The phenomenon of alpha decay is more evident while

filtering gases that contain liquid droplets or a mixture of liquid droplets and solid particles.

An exemplary dioctyl phthalate (DOP) challenge employs an automated filter testing unit purchased from TSI, Inc. equipped with an oil generator. The instrument
5 measures pressure drop across filter media and the resultant penetration value on an instantaneous or "loading" basis at a flow rate less than or equal to 115 liters per minute (lpm). An instantaneous test is defined as one set of penetration and simultaneous pressure drop reading. A "loading" is defined as a continuous series of pressure drop/penetration measurements, occurring approximately once every minute, until the desired
10 challenge is reached. The challenge is calculated by knowing the flow rate and mass concentration of the insulting agent, e.g., DOP.

In examples provided *infra*, a flow rate of 85 lpm and a test filter area of 170 cm² were used. The filtration media was placed within the instrument and closed for a 200 milligram DOP loading. The pressure drop and penetration values were recorded
15 approximately every minute until the desired loading was achieved. The final penetration and resistance value, as well as the overall efficiency decay, fell within the parameters established by NIOSH.

This DOP test is based on NIOSH standards as codified in 42 C.F.R. § 84 for filter classes where the three levels of filter efficiency are 95%, 99% and 99.97%.
20 Categories for resistance to filter efficiency degradation are N (not resistant to oil, e.g., DOP), R (resistant to oil) and P (oil proof). Therefore, nonwoven filter media of the present invention meet NIOSH classifications of R and preferably P 95 (95% oil proof by challenge), P 99 (99% oil proof by challenge) and P 100 (99.97% oil proof by challenge).

One of ordinary skill in the art will recognize the need to balance particle
25 penetration across a filter with the resistance to which the filter is subjected during filtration. In addition, it is also necessary to balance high initial alpha values with the alpha values after some degree of filtration challenge. The concentration of charge additives used according to the present invention as well as the identity of the charge additives can be varied to achieve optimal performance of electret filter media.

The term "within" refers to the condition in which a melt processable fatty acid amide is intimately dispersed throughout the fiber web fibers which make up the polymeric fiber web. For example, the melt processable fatty acid amide is thoroughly mixed with the polymer resin to form polymer pellets which are able to be extruded into
30

fibers which include the amide throughout the fiberous structure. Those having ordinary skill in the art will appreciate that the fatty acid amide can be incorporated into a polymer resin in a number of ways. In one example, the fatty acid amide can be combined with polymer resin using a two screw extruder, yielding pellets with a concentrated amount of 5 the amide. These concentrated pellets can then be combined with polymer pellets having no amide additive in an extrusion process that yields the desired polymer fiber web.

Filter efficiency and properties of the electret filter media of the invention can also be optimized through additional processing techniques. In one embodiment the polymer web, which has incorporated therein the charge stabilizing additive, can be heat treated 10 after the web is charged or treated to form a permanent dipole. Heat treating the web at this stage of the manufacturing process can enhance the charge stability in the resulting filter media. Heat treatment can usually be conducted at temperatures in the range of about 65° C to about 230° C, preferably between about 50° C to about 120° C, most preferably between about 60° C and about 90° C for approximately between about 15 15 seconds to about 5 minutes, more preferably between about 1 minute and about 2 minutes. Such a post-charging heat treatment technique is particularly useful to enhance filter performance.

Preferably, heat treatment is applied to the electret filter after charging or 20 formation of the permanent dipoles. Such heat treatment can result in a lower initial alpha, but the alpha values after a degree of filter loading tend to be higher than those achieved with filter materials that do not receive heat treatment. Heat treatment of the electret filter can be accomplished by methods known in the art, such as infrared heaters, microwave heaters, oil or water heated rollers, convention ovens. Preferably, the step of 25 heat treating, e.g., annealing, is performed by convection, thereby affording uniform annealing of the melt blown fiber web which contains the melt processable fatty acid amide within the web.

Heat treatment after charging is preferably conducted at temperatures in the range of about 65° C to about 230 °C, preferably between about 50° C to about 120° C, most 30 preferably between about 60° C and about 90° C for approximately between about 15 seconds to about 5 minutes, more preferably between about 1 minute and about 2 minutes. In general, the fatty acid amide appears to be more sensitive to the effects of post-charging heat treatment than are other classes of charge stabilizing additives. Thus, it is preferred that the filter media be subjected to post-charging heat treatment.

Methods to prepare plasma treated hydrophobic and/or oleophobic electret filter media are also part of the present invention. In one embodiment, the invention relates to a method for manufacturing melt blown hydrophobic and/or oleophobic plasma treated electret polymer media. A polymer web is treated with a plasma having hydrophobic and/or oleophobic reactive species, preferably with a plasma containing hexafluoropropylene reactive species. A web of melt blown polymer fibers is treated to form substantially permanent charge pairs or dipoles in the melt blown polymer web. The permanent dipoles can be imparted to the web by a variety of techniques including AC corona or DC corona discharge and combinations thereof as described *supra*. In a preferred embodiment, the manufacturing process can be modified by heat treating, e.g., annealing, the polymer web.

In another embodiment, the method includes manufacturing electret filter media by providing a web of melt blown polymer fibers having a charge stabilizing fatty acid amide incorporated within the fibers. The polymer web is treated with a plasma having hydrophobic and/or oleophobic reactive species, preferably a plasma containing hexafluoropropylene reactive species. The plasma treated web is exposed to AC and/or DC corona discharge to form substantially permanent charge pairs or dipoles in the melt blown polymer web. Typically the fatty acid amide is present in a range between about 0.01% and about 20%. In a preferred embodiment, the manufacturing process can be modified by heat treating, e.g., annealing, the polymer web.

One useful technique for processing the electret web of the invention is illustrated in Figure 1. As illustrated, the filter media can be prepared by forming, such as in an extruder 16, a web of melt blown polymer film from a polymer resin 12, such as polypropylene. The resin optionally includes, in concentrated form, a desired amount of the charge stabilizing additive 14, e.g., a fatty acid amide as described *supra*. The resulting web 18 can be attenuated at processing station 20, such as by drawing the fibers at a ratio of about 300:1. Thereafter, the web can optionally be subjected to charge treatment at station 22 (which can be an AC discharge unit, a DC corona discharge unit or combinations thereof) to form substantially permanent charge pairs or dipoles in the melt blown polymer web. In some instances it may be preferred to use an AC corona discharge unit followed by a DC corona discharge unit at processing station 22. Alternatively, charging can be effected using an AC corona discharge unit followed by one or more successive treatments in a DC corona discharge unit. Charging can also be

accomplished using other techniques, including friction-based techniques. The charged or uncharged web is plasma treated at station 24. The plasma treated electret fiber web is then subjected to one or more treatment(s) with AC and/or DC corona discharge at station 26.

5 Subsequent to forming and charging the electret filter media, and as noted above, the media can be subjected to heat treatment at station 28 to improve charge retention properties of the media. For example, heat treatment may take place at temperatures in the range of between about 60° C to about 90°C, for approximately 1 minute to about 2 minutes.

10 It is to be understood that various combinations of process steps are possible to achieve the desired plasma treated electret polymer web. That is, plasma grafting can be performed after an annealing step; corona discharge treatment can be performed after an annealing step; corona discharge can be performed prior to plasma treatment; and or an annealing step can be performed prior to either plasma treatment and/or treatment with 15 corona discharge(s). Preferably, the polymeric fiber web, with or without charge stabilizing agent(s), is plasma treated followed by treatment with AC and/or DC corona discharge, followed by a final annealing step.

The following examples serve to further described the invention.

Examples

20 Comparative Example 1, shown in Table I, evaluates a polypropylene melt blown filter web made on equipment built by J&M Laboratories, Dawsonville, GA. The melt blown is made of Exxon 3546G polypropylene resin with 1% Acrawax C from Lonza. The melt blown fiber web was made at a throughput of about 3 lb/hr/inch width at an average fiber diameter of about 3 microns, forming a 74 inch wide web.

25 The web was made on a lightweight polypropylene spunbound for support. The web was charged using two charge bars and two high voltage supplies from Simco. Charging was done at 60 feet per minute. One charge bar treated the top of the web at -26kV, 2.2mA. The other charge bar treated the bottom of the web at +28kV, 1.4mA. After charging, samples were tested for DOP loading.

30 A test used to determine whether the treatment is acceptable was to place approximately 1 milliliter of DOP or mineral oil drops across a web width. Treatment was determined to be acceptable when the drops remained on the surface of the web

indefinitely (due to treatment). If the web sample was not properly treated, the drops would penetrate the web instantly (untreated polypropylene) or within 5 minutes.

Example 1 – The melt blown web was made under identical conditions to Comparative Example 1. After melt blown production, a 36 inch fiber web was plasma treated with a process gas of hexafluoropropylene, no carrier gas, which ran at 3 lpm. The plasma was generated with 2000 watt RF power. The web was run through at 15 fpm which gave a 1 minute exposure time to the plasma gas. Uniformity of plasma treatment was assessed by the drop test using mineral oil as described above. The web was then tested with DOP loading. As demonstrated in Table I, it should be noted that Example 1 had alpha performance throughout the entire test which Comparative Example 1 reached after about 20 minutes of loading.

Example 2 – A melt blown fiber web was prepared as in Example 1 (melt blown and plasma treatment). The 36 inch plasma treated melt blown fiber web was then charged under the same conditions as in Comparative example 1 and then tested for DOP loading. As shown in Table I, initial performance values were the same as Comparative Example 1, but alpha decay much less.

TABLE I

DOP LOADING, 85 lpm, 170 cm² based on 42 CFR § 84 (170 cm² is the area of a typical molded disposable face mask)
4 plies of filter media

| Time min | EXAMPLE 1 PLASMA TREATED | | | EXAMPLE 2 PLASMA CHARGED | | | COMPARATIVE EXAMPLE I CHARGED | | |
|-------------|-----------------------------|-----------------------------------|-------|-----------------------------|-----------------------------------|-------|----------------------------------|-----------------------------------|-------|
| | Penetration % | Resistance mm H ₂ O | ALPHA | Penetration % | Resistance mm H ₂ O | ALPHA | Penetration % | Resistance mm H ₂ O | ALPHA |
| 0 | 16.3 | 15.4 | 4.8 | 0.059 | 14.1 | 20.6 | 0.052 | 15.6 | 20.6 |
| 5 | 12.7 | 13.2 | 5.7 | 0.052 | 14.6 | 18.9 | 0.54 | 12.8 | 14.4 |
| 10 | 11.3 | 16.3 | 5.8 | 0.094 | 17.3 | 17.5 | 1.33 | 16.3 | 11.5 |
| 15 | 10.4 | 16.4 | 6.0 | 0.12 | 18.3 | 16.0 | 3.54 | 18.0 | 8.1 |
| 20 | 9.8 | 17.1 | 5.9 | 0.137 | 18.3 | 15.6 | 8.8 | 18.1 | 6.3 |
| 25 | 9.3 | 17.7 | 5.8 | 0.139 | 18.2 | 15.4 | 7.54 | 18.6 | 5.7 |
| 30 | 8.9 | 17.7 | 5.9 | 0.207 | 19.0 | 14.1 | 6.63 | 20.2 | 5.3 |

Examples 3 to 7 (Table II, Table III and Table IV) – Samples of materials prepared in Example 2 were put into an oven at the temperatures noted in Tables II, III and IV for about 5 minutes and then tested for DOP loading. It was found that heat treatment reduces initial alpha, flattening decay curve of alpha values. Example 5 (150° F) has fairly "flat" DOP alpha curve through 30 minutes of loading (24 minutes

corresponds to 200 mg loading required for NIOSH masks). As heat treatment is increased, alpha performance decreases, and was found therefore not to be optimal for filter performance.

TABLE II

5 DOP LOADING 85 lpm, 170 cm²

4 plies

| | Time min | EXAMPLE 3 EX 2 Treated 110 ° F | | | EXAMPLE 4 EX 2 Treated 130 ° F | | |
|----|-------------|-----------------------------------|-----------------------------------|-------|-----------------------------------|-----------------------------------|-------|
| | | Penetration % | Resistance mm H ₂ O | ALPHA | Penetration % | Resistance mm H ₂ O | ALPHA |
| 10 | 0 | 0.811 | 13.4 | 15.6 | 1.47 | 14.9 | 12.3 |
| | 5 | 0.781 | 13.4 | 15.7 | 1.3 | 15.6 | 12.1 |
| | 10 | 0.832 | 14.1 | 14.8 | 1.35 | 16.5 | 11.3 |
| | 15 | 0.863 | 14.1 | 14.6 | 1.32 | 17.2 | 10.9 |
| 15 | 20 | 0.951 | 14.2 | 14.2 | 1.29 | 17.1 | 11.1 |
| | 25 | 1.02 | 14.8 | 13.5 | 1.35 | 17.5 | 10.7 |
| | 30 | 1.16 | 15.1 | 12.8 | 1.6 | 18.2 | 9.9 |

5 minutes at temperature

TABLE III

20 DOP LOADING 85 lpm, 170 cm²

4 plies

| | Time min | EXAMPLE 5 EX 2 Treated 150 ° F | | | EXAMPLE 6 EX 2 Treated 170 ° F | | |
|----|-------------|-----------------------------------|-----------------------------------|-------|-----------------------------------|-----------------------------------|-------|
| | | Penetration % | Resistance mm H ₂ O | ALPHA | Penetration % | Resistance mm H ₂ O | ALPHA |
| 25 | 0 | 2.38 | 14.7 | 11.0 | 5.35 | 13.3 | 9.6 |
| | 5 | 2.03 | 14.7 | 11.5 | 5.08 | 13.6 | 9.5 |
| | 10 | 1.83 | 15.2 | 11.4 | 4.75 | 14.2 | 9.3 |
| | 15 | 1.76 | 15.7 | 11.2 | 4.6 | 14.5 | 9.3 |
| 30 | 20 | 1.66 | 16.0 | 11.1 | 4.47 | 14.8 | 9.1 |
| | 25 | 1.62 | 16.2 | 11.1 | 4.29 | 14.7 | 9.3 |
| | 30 | | | | | | |

5 minutes at temperature

TABLE IV

35 DOP LOADING 85 lpm, 170 cm²

4 plies

| EXAMPLE 7 EX 2 Treated 190 ° F | | | | |
|-----------------------------------|-------------|------------------|-----------------------------------|-------|
| | Time min | Penetration % | Resistance mm H ₂ O | ALPHA |
| 5 | 0 | 7.73 | 13.1 | 8.5 |
| | 5 | 7.98 | 13.9 | 7.9 |
| | 10 | 7.71 | 14.0 | 7.9 |
| | 15 | 7.54 | 14.6 | 7.7 |
| | 20 | 7.15 | 14.9 | 7.7 |
| | 25 | 6.7 | 14.8 | 7.9 |
| 10 | 30 | | | |

5 Minutes At Temperature

15 Examples 8 (a to h) (Table V) -- Example 2 samples (plasma treated and charged) were heat treated in production equipment (IR heater oven). Oven temperature was set to achieve 150° F web temperature (using temperature indicating tapes) at a line speed of 15 fpm. This gave approximately a 45 second dwell time in the oven. Samples were layered up between 1 and 8 plies and then DOP loaded. Two plies met P 95
20 requirements, 3 plies met P 99 and 5 plies met P 100 requirements.

TABLE V

| | No. of Piles | Initial | | 24 minute Loading | | |
|----|-----------------|------------------|---|-------------------|------------------|---|
| | | Penetration % | Pressure Drop mm H ₂ O | ALPHA | Penetration % | Pressure Drop mm H ₂ O |
| 25 | 1 (8a) | 14.40 | 5.1 | 16.5 | 17.80 | 6.1 |
| | 2 (8b) | 2.40 | 10.1 | 16.0 | 3.21 | 12.6 |
| | 3 (8c) | 0.363 | 16.2 | 15.1 | 0.543 | 19.2 |
| | 4 (8d) | 0.167 | 20.9 | 13.3 | 0.180 | 24.1 |
| | 5 (8e) | 0.020 | 28.2 | 13.1 | 0.027 | 32.6 |
| | 6 (8f) | 0.006 | 34.4 | 12.3 | 0.007 | 38.6 |
| | 7 (8g) | 0.001 | 40.9 | 12.2 | 0.001 | 43.8 |
| | 8 (8h) | 0.001 | 47.0 | 10.6 | 0.001 | 50.5 |

35 Pressure drop in mm H₂O is an indication of breathability, as in a face mask, of the material. The lower the values, the less resistance there is in air passing through the material. Numerous samples demonstrate that the treated fiber webs of the invention

show very little pressure drop and can be used for face masks which would be comfortable to the wearer.

Those skilled in the art will know, or be able to ascertain, using no more than routine experimentation, many equivalents to the specific embodiments of the invention

5 described herein. These and all other equivalents are intended to be encompassed by the following claims. All publications and references cited herein including those in the background section are expressly incorporated herein by reference in their entirety.

What is claimed is:

1. A filter media comprising a melt blown oleophobic plasma treated electret polymer fiber web.

5

2. The filter media of claim 1, wherein said oleophobic plasma treatment is an oleophobic alkylene, acrylate, or methacrylate.

10 3. The filter media of claim 2, wherein said oleophobic alkylene, acrylate or methacrylate is halogenated.

4. The filter media of claim 3, wherein said halogen is fluorine.

15 5. The filter media of claim 3, wherein said halogenated alkylene is hexafluoropropylene.

6. The filter media of claim 1, wherein said filter media has a filter efficiency and degradation value of at least P 95.

20

7. The filter media of claim 1, wherein said polymer fiber web includes polymer fibers having a diameter in the range of between about 1 to 20 μm .

8. The filter media of claim 1, wherein the weight of said polymer fiber web is in the range of between about 10 to about 520 g/m².

25

9. The filter media of claim 1, wherein said fiber web is annealed.

10. A respirator having a filter element comprising a melt blown oleophobic plasma treated electret polymer fiber web as claimed in claim 1.

30

11. A respirator having a filter element comprising an annealed melt blown oleophobic plasma treated electret polymer fiber web as claimed in claim 9.

12. A filter media comprising a melt blown oleophobic plasma treated electret polymer fiber web having a melt processable fatty acid amide present within said web, wherein said amide is present at a concentration in a range from about 0.01% to about 20% by weight.

5

13. The filter media of claim 12, wherein said oleophobic plasma treatment is an oleophobic alkylene, acrylate, or methacrylate.

10 14. The filter media of claim 13, wherein said oleophobic alkylene, acrylate or methacrylate is halogenated.

15. The filter media of claim 14, wherein said halogen is fluorine.

15 16. The filter media of claim 14, wherein said halogenated alkylene is hexafluoropropylene.

17. The filter media of claim 12, wherein said filter media has a filter efficiency and degradation value of at least P 95.

20 18. The filter media of claim 12, wherein said polymer fiber web includes polymer fibers having a diameter in the range of between about 1 to 20 μm .

19. The filter media of claim 12, wherein the weight of said polymer fiber web is in the range of between about 10 to about 520 g/m^2 .

25

20. The filter media of claim 12, wherein said fiber web is annealed.

21. A respirator having a filter element comprising a melt blown oleophobic plasma treated electret polymer fiber web as claimed in claim 12.

30

22. A respirator having a filter element comprising an annealed melt blown oleophobic plasma treated electret polymer fiber web as claimed in claim 20.

23. A method for manufacturing melt blown oleophobic plasma treated electret polymer media comprising the steps of:

providing a web of melt blown polymer fibers;

treating said melt blown polymer web with an oleophobic plasma; and

treating said plasma treated web to form substantially permanent charge pairs or dipoles in said plasma treated melt blown polymer web, thereby forming melt blown oleophobic plasma treated electret polymer media.

5

24. The method of claim 23, wherein the oleophobic plasma contains

10 hexafluoropropylene.

15

25. The method of claim 23, further comprising the step of treating said oleophobic plasma treated electret polymer web at an elevated temperature, thereby annealing said resultant melt blown oleophobic plasma treated electret polymer media.

20

26. A method for manufacturing electret filter media having a charge stabilizing fatty acid amide comprising the steps of:

providing a web of melt blown polymer fibers having a charge stabilizing fatty acid amide incorporated within said fibers;

treating said melt blown polymer web with an oleophobic plasma; and

treating said oleophobic plasma treated web to form substantially permanent charge pairs or dipoles in said melt blown polymer web, thereby forming an oleophobic plasma treated electret polymer media having a charge stabilizing fatty acid present within the web.

25

27. The method of claim 26, wherein the oleophobic plasma contains hexafluoropropylene.

30

28. The method of claim 26, further comprising the step of treating said oleophobic plasma treated electret polymer web at an elevated temperature, thereby annealing said resultant blown oleophobic plasma treated electret polymer media.

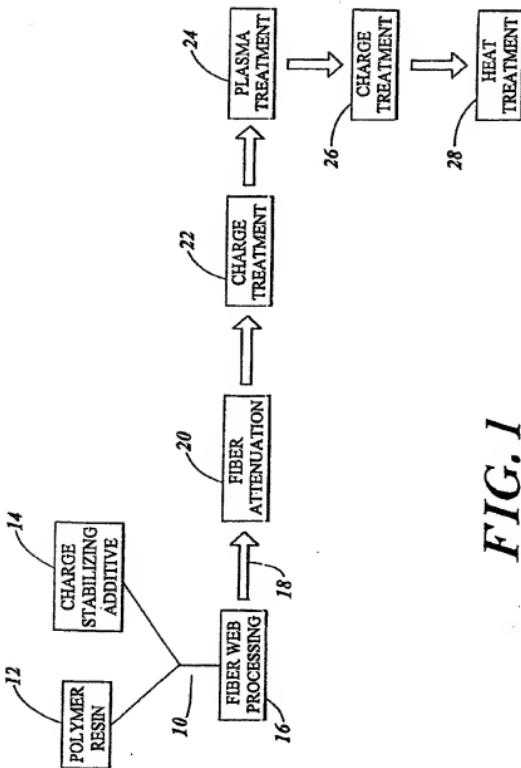


FIG. 1

INTERNATIONAL SEARCH REPORT

Interr. Application No.
PCT/US 00/19279

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01D39/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| A | US 5 645 627 A (N.LIFSHUTZ ET AL.) 8 July 1997 (1997-07-08) claims 1-10 ----- | 1,2,7-9, 12 |
| A | DATABASE WPI Week 198943 Derwent Publications Ltd., London, GB; AN 1989313601 XP002156374 & JP 01 232038 A (KURARAY CO LTD), 18 September 1989 (1989-09-18) abstract ----- | 1 |
| A | US 4 845 132 A (T.MASUOKA ET AL.) 4 July 1989 (1989-07-04) cited in the application claim 1 ----- -/- | 1 |

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

Date of the actual completion of the international search

29 December 2000

Date of mailing of the international search report

11/01/2001

Name and mailing address of the ISA

European Patent Office, P.O. 5818 Patentsteen 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-3040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Bertram, H

2

INTERNATIONAL SEARCH REPORT

| | |
|-----------------|---------------------|
| Intern | inal Application No |
| PCT/US 00/19279 | |

| C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|---|---|-----------------------|
| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| A | WO 99 16532 A (MINNESOTA MINING) 8 April 1999 (1999-04-08) claims 1,18 — US 4 407 852 A (S.W.SAPIEHA ET AL.) 4 October 1983 (1983-10-04) claim 1 — | 1 |
| A | | 1 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/19279

| Patent document cited in search report | | Publication date | | Patent family member(s) | | Publication date |
|--|---|------------------|--|---|--|--|
| US 5645627 | A | 08-07-1997 | | AU 4915496 A WO 9626783 A | | 18-09-1996 06-09-1996 |
| JP 1232038 | A | 18-09-1989 | | NONE | | |
| US 4845132 | A | 04-07-1989 | | JP 2062144 C JP 5070493 B JP 62262705 A CA 1313441 A DE 3769011 D EP 0249513 A KR 9008692 B | | 24-06-1996 05-10-1993 14-11-1987 09-02-1993 08-05-1991 16-12-1987 27-11-1990 |
| WO 9916532 | A | 08-04-1999 | | AU 6249498 A BR 9812585 A CN 1272069 T EP 1019173 A | | 23-04-1999 25-07-2000 01-11-2000 19-07-2000 |
| US 4407852 | A | 04-10-1983 | | CA 1141020 A DE 3039561 A JP 1057490 B JP 1569774 C JP 56103415 A | | 08-02-1983 02-07-1981 06-12-1989 10-07-1990 18-08-1981 |